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THE EFFECT OF SUBSTITUTING ATOMS OF HYDROGEN  
IN THE  $\text{CH}_3\text{Br}$  MOLECULE WITH ATOMS OF BROMINE  
ON THE VELOCITY OF THE IONIC ISOTOPE EXCHANGE

- USSR -

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THE EFFECT OF SUBSTITUTING ATOMS OF HYDROGEN  
IN THE  $\text{CH}_3\text{Br}$  MOLECULE WITH ATOMS OF BROMINE  
ON THE VELOCITY OF THE IONIC ISOTOPE EXCHANGE

[Following is a translation of an article  
by M. B. Neyman, Yu. M. Shapovalov, and  
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Since the time of the appearance of the classical dissertation of V. V. Markovnikov [1], a considerable number of works have been published dedicated to the study of the mutual effect of atoms on the reaction ability of the molecule.

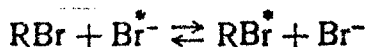
Unfortunately, the great majority of works in this area are of a qualitative character. In the present work, we carried out a quantitative investigation of the effect of substituting atoms of hydrogen in the molecule of  $\text{CH}_3\text{Br}$  with atoms of bromine on the velocity and the energy of activation of isotope exchange of bromine-substituted methane with bromine ions in a 90% alcohol solution. The pattern of reaction of the isotope exchange selected by us for the study of the reaction capability possesses a series of advantages over those employed by B. V. Tarnov [2] for the same purpose, namely reactions of emulsification and esterification.

Indeed, the thermal effect of reactions of the isotope exchange is equal to zero, and therefore the equilibrium constant does not depend on temperature. Besides, these reactions are fully reversible and their course is not connected with the formation of side products.

Therefore, the experimental material during study of the isotope exchange reactions can be easily treated so that the velocity constants and the energy of activity can be determined without difficulty (3, 4).

The compounds  $\text{CH}_3\text{Br}$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$  and  $\text{CBr}_4$  were purified by distillation or recrystallization and, after that, their physical constants coincided with table values within the limits of allowable error.

Reactions of the isotope exchange



were carried out in sealed flasks placed in a thermostat. In all experiments, the concentration of both compounds was equal to 0.1 eq/l. At different times, the flasks were cooled and then opened. In the case of experiments with  $\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_3$  the separation of compounds was carried out by an addition of water and cyclohexane as was described earlier (5). In the case

In the case of experiments with  $\text{CH}_3\text{Br}$ , the latter together with alcohol was driven off from the trap at low pressure, after which the activity of  $\text{NaBr}$  left in the trap was determined. In the case of experiments with  $\text{CBr}_4$  the solvent also was driven off from the trap at low pressure and a temperature below zero; that is, at such conditions when the isotope exchange can be neglected.  $\text{CBr}_4$  was extracted from the solid residue with ether and after that  $\text{NaBr}$  was dissolved in water.

For measurements of activity, in all cases the bromine was transferred into  $\text{AgBr}$  residue as was described in previous works.

A series of experiments were carried out for each temperature and the velocity constants were calculated according to the formula:

$$K = -\frac{2.3}{(a+b)ft} \lg \left[ 1 - \left( 1 + \frac{b}{a} \right) \frac{x}{c} \right]. \quad (1)$$

The formula is applicable in the case of molecular-ion mechanism of the isotope exchange reactions according to which reactions take place, as was shown by us earlier (6).

The results of our experiments are given in Table 1. In the table are quoted mean values of constants in 1 mole sec. In all cases, the  $f$ -activity coefficient of  $\text{NaBr}$  was accepted as being equal to 0.7 as follows from our measurements (6).

Fig. 1 represents the relation between the velocity constants of the isotope exchange determined by us and the temperature. As is apparent from the drawing, during the transition from  $\text{CH}_3\text{Br}$  to  $\text{CH}_2\text{Br}_2$  the velocity of the isotope exchange is sharply decreased. An introduction into the molecule of one atom of bromine, that is, a transition to  $\text{CH}_2\text{Br}_2$ , has a very limited effect on the velocity exchange.

Table 1

Velocity Constants of the Isotope Exchange  $RBr + Br^- + Br^{*-}$  at  $a = b = 0.1$  eq/l

RBr	T, °C	$K \cdot 10^3$	RBr	T, °C	$K \cdot 10^3$
CH <sub>3</sub> Br	19,7	9,4	CHBr <sub>3</sub>	100	3,1
	37,0	97,0		110	13,1
	50,8	199,0		120	24,0
CH <sub>2</sub> Br <sub>2</sub>	115,8	19,0	CBr <sub>4</sub>	140	130,0
	130	71		100	23
	152	348		110	53
				120	79
				140	330

Table 2

Kinetics Characteristics of the Isotope Exchange  
 $CH_nBr_{4-n} + Br^{*-}$ .

RBr	$K_{100} \cdot 10^5$ $L \cdot mol^{-1} \cdot sec^{-1}$	$E$ , cal/mol
CH <sub>3</sub> Br . . .	5420	17500
CH <sub>2</sub> Br <sub>2</sub> . .	3,1	26600
CHBr <sub>3</sub> . . .	3,2	28000
CBr <sub>4</sub> . . . .	16	20300

Finally, the transition to  $\text{CBr}_4$  not only does not delay the isotope exchange but leads to its acceleration.

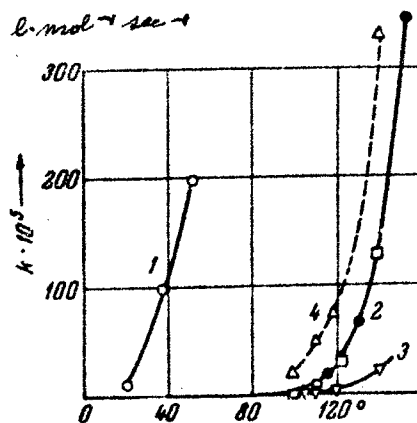


Fig. 1. The relationship of the temperature on the velocity constant of the isotope exchange: I-1

- 1) with  $\text{CH}_3\text{Br}$ ;
- 2) with (points) and  $\text{CH}_2\text{Br}_2$  (squares);
- 4) [sic] with  $\text{CBr}_4$

Curve 3 indicates temperature effect on the exchange constant  $K_1$  according to ionizing mechanism.

For determination of the active energy of the studied reactions of isotope exchange, we expressed the results of our experiments in Fig. 2 in terms of coordinates  $\lg K$  and  $1/T$ . Calculated by a method of least squares, the values of the energy of activation and the velocity constant of the isotope exchange are compared in Fig. 2.

As is clear from the table, during the transition from  $\text{CH}_3\text{Br}$  and  $\text{CHBr}_3$ , the velocity of isotope exchange diminishes and the energy of activation grows. At the introduction into the molecule of the fourth atom of bromine, the regularity is disturbed as was observed in the case of other reactions but left without explanation by P. I. Petrenko-Kritchenko (7) and B. V. Tronov (2). It is possible therefore to theorize that in the case of  $\text{CBr}_4 + \text{Br}^+$  the isotope exchange proceeds according to a different mechanism.

As was demonstrated by us, the isotope exchange of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$  with ions of  $\text{Br}^{*-}$  proceeds according to a molecular-ion mechanism (6). The reaction is accompanied with inversion of configuration and its velocity constant must be calculated by formula (1).

It is very probable that in the case of polyhalide substitutes, the mutual repulsion of halide atoms may lead to a marked increase of the process of molecular ionization and, as a result, the process of the isotope exchange will proceed according to an ion-type mechanism. In this case, the velocity exchange constant should be calculated not according to formula (1) but according to formula (2):

$$K' = -\frac{2,3b}{(a+b)t} \lg \left[ 1 - \left( 1 + \frac{b}{a} \right) \frac{x}{c} \right]. \quad (2)$$

To substantiate this theory, we arranged a series of experiments concerning the study of kinetics of the isotope exchange  $\text{CBr}_4 + \text{NaBr}^*$  in alcohol solutions at  $100^\circ$ . The concentration of the reacting substances fluctuated within wide limits. The results of our experiments are given in Table (3):

Table 3

Constants of Isotope Exchange

$\text{CBr}_4 + \text{NaBr}^*$				
$a, \frac{\text{mol}}{\text{L}}$	$b, \frac{\text{mol}}{\text{L}}$	$K \cdot 10^3, \frac{\text{L} \cdot \text{mol}^{-1}}{\text{sec}^{-1}}$	$K' \cdot 10^3, \frac{\text{L} \cdot \text{mol}^{-1}}{\text{sec}^{-1}}$	$K'' \cdot 10^3, \frac{\text{L} \cdot \text{mol}^{-1}}{\text{sec}^{-1}}$
0,5	0,6	3	0,8	1,4
0,9	0,1	20	1,3	13
0,99	0,01	330	3	300

The constant K was calculated according to formula (1), the constant  $K'$  according to formula (2), and the constant  $K''$  according to the following formula (3):

$$K'' = -\frac{2,3}{(a+b)t} \lg \left[ 1 - \left( 1 + \frac{b}{a} \right) \frac{x}{c} \right], \quad (3)$$

which is related to the case of a molecular mechanism of the reaction process.

As is apparent from the table, during the change of concentration of  $\text{NaBr}$  by a factor of 60, the constants K and  $K''$  change by a factor of 100 to 200, but the constant  $K'$  changes only by a factor of 4.

It follows from our experiments that for the reaction of the isotope exchange  $\text{CBr}_4 + \text{Br}^{*-}$ , the mechanical-ion exchange process appears to be most probable.

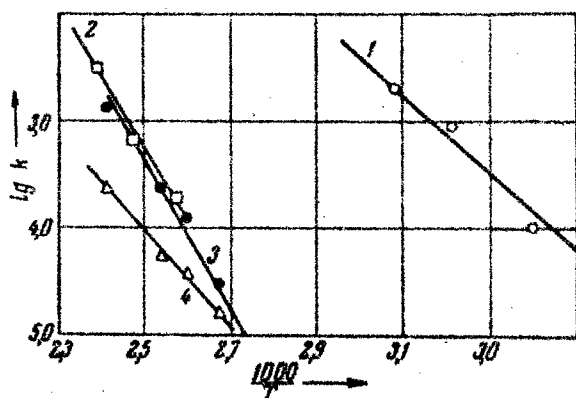


Fig. 2. Relationship between temperature  $\lg k$  and the ion reaction of the isotope exchange  $\text{CH}_3\text{Br}$  (1),  $\text{CH}_2\text{Br}_2$  (2),  $\text{CHBr}_3$  (3)  $\neq$   $\text{CBr}_4$  (4).

Therefore, the velocity constant of the reactions  $\text{CBr}_4 + \text{Br}^{*-}$  in agreement with our experimental data must be expressed by formula:

$$K' = 1,3 \cdot 10^7 \cdot e^{-203000/RT}. \quad (4)$$

The relationship between  $K'$  and temperature, calculated according to this formula, is presented in Figs. 1, 3, where on the ordinate axis are given the values of the constant in  $\text{sec}^{-1}$ , in scale previously used.

Our experiments lead to the conclusion that the isotope exchange of halides with ions of halides proceeds according to a molecular-ion mechanism accompanied with inverse configuration and not according to the ion-type mechanism. In general, one of these mechanisms prevails. In the case of gradual substitution of atoms of hydrogen in the molecule  $\text{CH}_3\text{Br}$  with bromine atoms, the potential barrier hindering inversion of the configuration rises monotonously.

However, at the same time, the potential barrier decreases the same barrier which impedes decomposition of molecules on the negative ion of bromine and the positive ion of carbonium.

Due to this circumstance, the competition of the molecular-ion and the ionization mechanisms leads in the case of  $\text{CH}_3\text{Br}$  to the second mechanism. Analogous ideas with reference to mechanisms of some other ionic reactions were expressed by Ingold (8).

In our of our works (9), it was demonstrated that a change in structure that causes retardation of the ion reactions at the same time accelerates the atom reactions of the isotope exchange. From this point of view, we must expect acceleration of the isotope exchange  $\text{CH}_n\text{Br}_{4-n}$  with atoms of bromine in proportion to the reduction of  $n$ .

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